Generalized-master-equation theory of excitation transfer*

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(Received 11 February 1974)

A theory of the time dependence of resonance transfer of excitation energy between molecules is developed in terms of memory functions appearing in the transition rates of a generalized master equation (GME). The memory can be computed explicitly and, due to the coarse-graining operation incorporated in our derivation of the GME, the accuracy of the memory function depends only on the amount of detailed information one has, or wishes to include, about the spectrum and dynamics of the system. The formalism yields a unified description of coherent motion at short times and diffusive transport at long times, and for the case of transfer between and among identical molecules provides a generalized approach to the theory of exciton transport. Memory functions for transfer between anthracene molecules are obtained as an illustration of the theory. The connection between the new formalism and existing exciton-transport theories is indicated and its relation to the theory of non-Markoffian random walks is presented.

I. INTRODUCTION

Exciton transport plays a role wherever a transfer of electron excitation energy from one spatial location to another takes place without an accompanying particle transfer. An extensive review of exciton-diffusion phenomena in organic solids has been recently published by Birks.[1] Sensitized luminescence has been an active field of solid-state research[2] for a long time. The biological process of photosynthesis provides yet another example of such energy transfer.[3] When light is incident on a photosynthetic system, it is absorbed and the impinging photons are converted into excitons. Reaction centers capable of utilizing the energy in these excitons exist however only at certain locations in the system and a transfer of the excitation from the absorbing sites to the reaction centers must therefore take place before the photosynthetic reaction can begin. The investigation of excitation transfer is therefore of importance in diverse fields of study and much theoretical work has been done in this area. Förster[4] developed a diffusion equation and computed the rates of excitation transfer between molecules. Dexter[5] extended the transfer-rate calculation to cases of dipole-forbidden transitions and with Schulman[6] applied it to the kinetics of various processes mainly in the inorganic realm. Trlifaj[7] further developed the diffusion equation, and several others, beginning with Bay and Pearlstein, have applied it (or an equivalent dynamics) to biological problems.[8] A wealth of detail is available on the exciton-diffusion tensor in polyacene crystals, much of it due to Avakian and co-workers.[9] However as these authors pointed out, an inaccurate microscopic model for the exciton propagation could reproduce the correct diffusion behavior on a macroscopic scale and great care must therefore be exercised in drawing conclusions concerning the microscopic motion of

excitons, which are based on the diffusion equation.

Recently the question of how and under what conditions diffusion theory must be replaced by a more accurate theory has been raised and answered quantitatively to varying degrees. A unified treatment of "excitonic" (wavelike) and "Förster" (diffusive) transfer is an old problem which has received increasing attention.[10-13]

In this paper we investigate the problem of excitation transfer with the help of a formalism based on generalized master equations (GME). The GME is introduced in Sec. II as the point of departure for transport calculations and it is indicated how a unified description of coherent and incoherent motion can be given with its help by making use of its non-Markoffian character. In Sec. III, coarse graining is introduced through a modification of the Zwanzig projection operators and explicit expressions for the memory-possessing transition rates in the GME are presented. The theory is then applied to excitation transfer between like as well as unlike molecules in Secs. IV and V, expressions connecting the transition rates to optical spectra being given in Sec. V. These two sections provide a generalization of Förster's well-known theory.[4] A discussion including a comparison of our formalism to existing theories of exciton transport and the connection of our theory to the formalism of continuous-time random walks is presented in Sec. VI.

II. GENERALIZED MASTER EQUATIONS

Transport theory traditionally employs the Pauli master equation as its point of departure. An important problem of nonequilibrium statistical mechanics is therefore the clarification of the connection between this equation and the Schrödinger equation satisfied by the system constituents at the microscopic level. Several authors[14-17] have at-

tempted this problem and, as an intermediate step in such derivations, have obtained non-Markoffian equations obeyed by the system probabilities. These equations are known as generalized master equations (GME). Among the various methods for obtaining the GME the procedure of Zwanzig[16] distinguishes itself by its elegance and economy of effort. Starting from the Liouville–von Neumann equation for the density matrix ρ

$$i\frac{\partial\rho}{\partial t} = [H, \rho] \equiv L\rho \tag{1}$$

(where $\hbar = 1$), one arrives at

$$\frac{\partial P_\xi(t)}{\partial t} = \int_0^t ds \sum_\mu \left\{ \mathcal{W}_{\xi\mu}(t-s)P_\mu(s) - \mathcal{W}_{\mu\xi}(t-s)P_\xi(s) \right\}$$

$$+ \mathcal{I}_\xi(t) \quad, \tag{2}$$

where L is the Liouville operator, H is the system Hamiltonian which is decomposed through

$$H = H_0 + V \quad, \tag{3}$$

ξ, μ are eigenstates of H_0, and $P_\xi \equiv \langle \xi | \rho | \xi \rangle$ is the diagonal element of ρ in the representation of H_0 eigenstates; it represents the probability of occupation of the states ξ. The projection operators employed in the derivation of (2) from (1) are defined through the relation

$$\mathcal{P}O = O_d, \text{ for any operator } O, \tag{4}$$

where O_d is the part of O diagonal in the representation of the H_0 eigenstates. As explained in Ref. 16, the operators $\mathcal{P}$, L etc. can be represented by tetradics and the $\mathcal{W}_{\xi\mu}$ and $\mathcal{I}_\xi$ in (2) have the following exact expressions:

$$\mathcal{W}_{\xi\mu}(t) = -\left\{ \mathcal{P}Le^{-it(1-\mathcal{P})L}(1-\mathcal{P})L \right\}_{\xi\xi\mu\mu} \quad, \tag{5}$$

$$\mathcal{I}_\xi(t) = i\left\{ \mathcal{P}Le^{-it(1-\mathcal{P})L}(1-\mathcal{P})\rho(0) \right\}_{\xi\xi} \tag{6}$$

Under the initial-diagonality condition

$$\rho(0) = \rho_d(0) \quad, \tag{7}$$

Eq. (6) forces $\mathcal{I}_\xi(t)$ to be zero and one obtains

$$\frac{\partial P_\xi(t)}{\partial t}$$

$$= \int_0^t ds \sum_\mu \left[\mathcal{W}_{\xi\mu}(t-s)P_\mu(s) - \mathcal{W}_{\mu\xi}(t-s)P_\xi(s) \right] \quad. \tag{8}$$

This is the GME. While it normally serves as only an intermediate step in the derivation of the Pauli master equation (PME), we shall use it (in fact a different form of it obtained by a modification of the operator $\mathcal{P}$) as our point of departure in transport calculations.

The only formal difference between the GME (8) and the PME below,

$$\frac{\partial P_\xi(t)}{\partial t} = \sum_\mu [F_{\xi\mu} P_\mu(t) - F_{\mu\xi} P_\xi(t)] \quad, \tag{9}$$

is that the transition probabilities $F_{\xi\mu}$ in (9) are time independent while their counterparts $\mathcal{W}_{\xi\mu}(t)$ in (8) are non-Markoffian. However, this very difference makes it possible for the GME (8) to provide a description of transport phenomena that lie outside the reach of the PME (9).

The passage from (8) to (9) in Refs. 15–17 makes the use of the Markoffian approximation, which consists, in general, of replacing an equation of the kind

$$A(t) = \int_0^t ds\, B(t-s)C(s) \tag{10}$$

by

$$A(t) = \left(\int_0^\infty ds\, B(s) \right) C(t) \tag{11}$$

which involves replacing $B(t)$ by

$$\left(\int_0^\infty ds\, B(s) \right) \delta(t) \quad.$$

Whatever the finer details of the argument may be, the derivation of the PME (9) from the GME (8) therefore consists of assuming a δ-function-like $\mathcal{W}_{\xi\mu}(t)$. It must be emphasized that this passage from (8) to (9) does *not* hold for all interactions and for all times and its validity is claimed only for certain V's and only on a certain time scale (see Refs. 15–17). Also, given a particular system, the analysis in Ref. 16 does not provide one with a criterion to decide whether or not the transition from (8) to (9) or equivalently the perfect absence of memory in $\mathcal{W}_{\xi\mu}(t)$ is valid for the given system. Van Hove has emphasized[15] that certain interactions V may only lead to a "dressing" of the H_0 states and cause no approach to equilibrium and therefore be incompatible with a master equation of the type of Eq. (9). An example may be easily given. If H_0 represents free electrons (noninteracting among themselves) a V arising from impurity scattering or phonon scattering may lead to an irreversible behavior and to Eq. (9) but one arising from a periodic Bloch potential will only lead to a dressing of the electrons with a transition of the free states into Bloch states. No irreversible behavior will be present in this case and Eq. (9) will *not* be obtained.

The relevance of the immediately preceding discussion to the present problem lies in the conclusion that the assumption

$$\mathcal{W}_{\xi\mu}(t) = F_{\xi\mu}\delta(t) \tag{12}$$

that is made to obtain Eq. (9) from Eq. (8) may not always be appropriate. In fact it is valid only in a limiting sense, and is responsible for "washing

out" a considerable amount of the *reversible* be-
havior of a system which may be important in a
particular situation. In fact, it is this reversible
part of the behavior of the system that leads to the
wavelike transport of excitons but an assumption
like Eq. (12) eliminates it entirely causing it to be
absent in Eq. (9).

A study of the exact expression for $\mathcal{W}_{\xi\mu}(t)$ shows
that the memory is actually oscillatory or some-
times even time independent. This is a conse-
quence of the reversible nature of the microscopic
equation and it makes the GME (8) *incompatible*
with the PME (9). However, as will be shown be-
low, a coarse-graining operation introduced to
represent the passage from the microscopic to the
macroscopic level of description causes the re-
sulting $\mathcal{W}$'s to decay in time. If τ is a character-
istic time of $\mathcal{W}(t)$, i.e., if $\mathcal{W}(t)$ tends to zero for
$t \gg \tau$, the PME (9) is able to provide an accurate
description of transport for large times while the
GME (8) must be used for $t < \tau$ and $t \sim \tau$. The sim-
ple physical picture that emerges from the detailed
analysis in terms of the GME is that the exciton
(or any other quasiparticle undergoing transport)
hops from site to site but pauses at each site be-
tween hops. In the case of excitons this pausing
may be said to come about due to the exciton-pho-
non interaction. The pausing time is represented
by τ and for excitons $\tau \sim 10^{-12}$ sec in most systems
of interest. The physical meaning of the relation-
ship between the PME (9) that is traditionally used
for transport calculations and the GME (8) that we
propose to use is therefore quite transparent. The
PME assumes the pausing time τ to be essentially
zero. The GME (8) can·thus probe into transport
phenomena at times shorter than τ while the PME
(9) gives a coarser description "smoothed" over
such times.

The details of our modification of $\mathcal{P}$ and our new
GME will be given in the following sections. We
shall end this section with a few remarks about a
simplified form of Eq. (8). While transport theory
should really start from Eq. (8) in its full com-
plexity, a simplification may often be possible
whereby the time dependence of $\mathcal{W}_{\xi\mu}$ is assumed
independent of the states ξ and μ:

$$\mathcal{W}_{\xi\mu}(t) = F_{\xi\mu}\phi(t) \quad . \tag{13}$$

This reduces Eq. (8) to the simpler form

$$\frac{\partial P_{\xi}(t)}{\partial t} = \int_0^t ds\,\phi(t-s)$$

$$\times \sum_{\mu}[F_{\xi\mu}P_{\mu}(s) - F_{\mu\xi}P_{\xi}(s)] \quad . \tag{14}$$

The nature of the transport is then decided by the
memory $\phi(t)$ as well as by the rates $F_{\xi\mu}$.

A simple example will clearly show how the

GME formalism can provide a unified formulation
of wavelike and diffusive transport. Consider a
quasiparticle undergoing transport in two different
limits: the wave limit

$$\frac{\partial^2 P(x,t)}{\partial t^2} = c^2 \frac{\partial^2 P(x,t)}{\partial x^2} \tag{15}$$

[where the proper initial conditions are taken so
that positivity of $P(x,t)$ is assured throughout its
evolution] and the diffusive limit

$$\frac{\partial P(x,t)}{\partial t} = D \frac{\partial^2 P(x,t)}{\partial x^2} \quad . \tag{16}$$

As is well known,[18] the characters of the motion
predicted by (15) and (16) are combined into the
solutions of

$$\frac{\partial^2 P(x,t)}{\partial t^2} + \frac{c^2}{D}\frac{\partial P(x,t)}{\partial t} = c^2 \frac{\partial^2 P(x,t)}{\partial x^2} \quad , \tag{17}$$

which is a particular case of the telegrapher's
equation.[18] On making the nearest-neighbor ap-
proximation on the F's in (14) and taking the con-
tinuum limit, the GME (14) reduces to

$$\frac{\partial P(x,t)}{\partial t} = \int_0^t ds\,Q(t-s)\frac{\partial^2 P(x,s)}{\partial x^2} \quad , \tag{18}$$

where the F's have been assumed symmetric (no
bias). It is straightforward to write the memory
$Q(t)$ in (18) in terms of the F's and the $\phi(t)$ in (14).
It is now seen that (15) and (16) can be obtained
immediately from (18) on taking the respective
forms $Q(t) = c^2\theta(t)$ and $Q(t) = D\delta(t)$ for the memory
function. Furthermore (17) which constitutes a
unification of (15) and (16) is obtained from (18)
on assuming that the memory in $Q(t)$ is neither per-
fect as in the case of (15) not completely absent
as in (16) but has the intermediate form $Q(t)$
$= c^2 e^{-(c^2/D)t}$.

III. COARSE GRAINING

The quantity basic to the approach suggested in
this paper is the memory-possessing "transition
rate" $\mathcal{W}_{\xi\mu}$ appearing in the GME (8). It connects
the probability at a "site" μ and at a time s in the
past to the rate of change of the probability at the
"site" ξ at the present time t. An expression for
it appears in Eq. (5) where it is given in terms of
elements of tetradics corresponding to the opera-
tors L, $\mathcal{P}$, etc. Following Zwanzig[16] we can obtain
an approximate expression for $\mathcal{W}_{\xi\mu}$ by replacing L
by L_0 in the exponential in Eq. (5). The latter de-
notes commutation only with the part H_0 of the full
Hamiltonian H. Observing that ξ, μ are eigen-
states of H_0 it is straightforward to show that Eq.
(5) reduces to

$$\mathcal{W}_{\xi\mu}(t) = 2|V_{\xi\mu}|^2 \cos(E_\xi - E_\mu)t \quad , \tag{19}$$

where E_ξ and E_μ are eigenvalues of H_0 and $V_{\xi\mu}$

$= \langle \xi | V | \mu \rangle$. As discussed by Zwanzig,[16] (19) is the first term in a systematic perturbation expansion and the higher-order terms, if difficult to display explicitly, can be at least written down formally. An idea of what is involved in this approximation may be obtained by comparing the approximate and the exact expressions for $\mathcal{W}_{\xi\mu}$ calculated for a simple soluble model. This has been done in Appendix A where it is seen that the exact and the approximate expressions are identical to each other except for a first-order correction to the difference in the frequency of the cosine function in Eq. (19). While the complete expression for $\mathcal{W}_{\xi\mu}$ is given by Eq. (5), an exact evaluation of it would be tantamount to the full solution of the dynamical problem. Except for a few (drastically simplified) exactly soluble models, such a solution is quite out of the question. For this reason the approximate expression (19) will be used in the rest of this paper.

The reduction of the GME (8) to the PME (9) with its rates $F_{\xi\mu}$ described by the golden rule can be immediately done with the help of the Markoffian approximation discussed in Eqs. (10)–(12). For the replacement of $\int_0^\infty dt \cos(E_\xi - E_\mu)$ by $\pi\delta(E_\xi - E_\mu)$ indeed yields the golden rule.

Inspection of Eq. (19) shows that, as one might expect, the basic microscopic form of $\mathcal{W}_{\xi\mu}$ is oscillatory and nondecaying. Since an irreversible description of transport and an eventual passage into the Pauli master equation necessitate a decaying memory, one requires a coarse-graining operation representing the passage from the microscopic to the macroscopic level of description. For this purpose we modify the Zwanzig projection operator in such a way that it incorporates the coarse-graining operation. The operator $\mathcal{P}$ acting on an arbitrary operator O now erases all off-diagonal elements of O and replaces the diagonal elements by their averages over the regions over which the coarse graining is carried out. The microscopic states will now be denoted by ξ' and μ' and the macroscopic states (equivalently the sets of ξ', μ', etc. over which the coarse-graining is carried out) by the original state labels ξ, μ, etc. In this notation

$$\langle \xi' | \mathcal{P}O | \mu' \rangle = \langle \xi' | O | \xi' \rangle \delta_{\xi'\mu'} \equiv O_{\xi'\xi'}\delta_{\xi'\mu'}$$

for the Zwanzig operator but

$$\langle \xi' | \mathcal{P}O | \mu' \rangle = \left\{ \sum_{\xi''\subset\xi} O_{\xi''\xi''} \Big/ \sum_{\xi''\subset\xi} 1 \right\} \delta_{\xi'\mu'}$$

for our modified operator. The coarse-graining sums run over all states ξ' within the "grains" ξ. The label ξ often provides a complete description of a state in a subspace of the system: $|\xi'\rangle = |\xi\rangle \otimes |a\rangle$. The sum over $\xi' \subset \xi$ is then a sum over all states $|a\rangle$. With the new definition of the pro-

jection operator it is possible to derive a modified GME which is formally identical to (8) with its $\mathcal{W}$'s and $\mathcal{S}$'s given by (5) and (6). The explicit expression for $\mathcal{W}_{\xi\mu}$ at the same level of approximation as (19) is, however, after some calculation

$$\mathcal{W}_{\xi\mu}(t) = 2 \sum_{\substack{\xi'\subset\xi \\ \mu'\subset\mu}} |\langle \xi' | V | \mu' \rangle|^2 \cos(E_{\xi'} - E_{\mu'})t \quad (20)$$

and the GME describes transport in the *coarse-grained* space of the ξ, μ states. Using $|\xi'\rangle = |\xi\rangle \otimes |a\rangle$ which is particularly appropriate when the description is in terms of a bath whose states are the a's, one has

$$\mathcal{W}_{\xi\mu}(t) = 2 \sum_{a,b} |\langle \xi,a | V | \mu,b \rangle|^2$$
$$\times \cos\omega_{ab}t \, \cos\Omega_{\xi\mu}t$$

minus a similar term with sine functions, the ω_{ab} and $\Omega_{\xi\mu}$ being energy differences of the bath and the (coarse-grained) system, respectively. The memory possessing "transition probability" $\mathcal{W}_{\xi\mu}(t)$ is thus seen to emerge (except for the $\cos \Omega_{\xi\mu}t$ factor) as the Fourier transform of the interaction

$$|\langle \xi,a | V | \mu,b \rangle|^2 \quad .$$

One at once sees how the decaying macroscopic memory arises out of and in spite of the basic oscillatory memory at the microscopic level. The cosines $\cos \omega_{\xi'\mu'}t$ at the microscopic level serve in Fourier transforming the interaction V. The basic oscillatory character of the memory is still seen at the macroscopic level through the $\cos\Omega_{\xi\mu}t$ factor but the time dependence of $\mathcal{W}_{\xi\mu}$ is dominated by the nature of V. It should be noticed that our present analysis provides a means of knowing whether a given V will lead merely to a "dressing" of the H_0 states and cause no approach to equilibrium or whether it will result in an irreversible behavior of the kind described by the master equation. This information which was absent in previous investigations[16] of the problem of irreversibility carried along these lines,[19] is contained in the Fourier transform of

$$|\langle \xi' | V | \mu' \rangle|^2 \quad .$$

The present analysis can thus be used for an investigation of the irreversibility problem. However the details are not particularly relevant to the phenomenon of exciton transport and will therefore be presented elsewhere.[20]

IV. EXCITATION TRANSFER BETWEEN MOLECULES

So far the fact that the entity whose transport is being studied is an exciton has not entered into the picture. The analysis can as well be applied for instance to study the motion of electrons in an amorphous solid. We shall now restrict our atten-

tion specifically to the problem of exciton transport.

Let us consider transfer of excitation energy among a group of identical molecules. A state ξ will be represented as M, m where M refers to the site at which the exciton (the excited state) is, and m represents the vibrational states. For simplicity only two electronic states (the ground and the excited state) will be assumed to exist at each site, a trivial restriction which is easily relaxed. The GME (8) thus takes the form

$$\frac{\partial P_{M,m}(t)}{\partial t} = \int_0^t ds \sum_{N,n} [w_{M,m\,N,n}(t-s)P_{N,n}(s) - w_{N,n\,M,m}(t-s)P_{M,m}(s)] \; . \tag{21}$$

The terms on the right-hand side of this equation with $N=M$ represent intramolecular relaxation whereas those with $N \neq M$ denote intermolecular transfer and relaxation. The Förster-Dexter analysis is equivalent to making two approximations in Eq. (21): (i) replacing $w(t)$ by $[\int_0^\infty dt \; w(t)]\delta(t)$ and (ii) replacing $P_{N,n}(s)$ by $P_N(s)P_n^{th}$, where $P_N(s) = \sum_n P_{N,n}(s)$. Here $P_N(s)$ refers to the probability that the excitation is at site N no matter what its vibrational state and P_n^{th} is the thermalized distribution among vibrational states. Assumption (i) is the Markoffian approximation discussed earlier and is the one responsible for washing out all wavelike behavior. Assumption (ii) insists that thermalization occurs before transfer and makes it impossible for "fast" or "hot" transfer to be described by the formalism.

The Förster analysis[4] is unable to study problems such as hot transfer since the PME, which is its starting point, is already in a highly coarse-grained space. Information in vibrational states m, n, etc, is integrated out leaving only a description in the space of M, N, etc. In other words, the transitions described in the Förster approach are from sites N to sites M and not from states N, n to states M, m. Our present analysis is quite capable of treating the problem of transitions of the latter kind. To make contact with the Förster theory however, we shall first show what the new predictions of our analysis are at its own (coarse) level of description. For this purpose we redefine the projection operator in such a way that it coarse grains over m, n, etc. as well as over a, b, etc. which might represent vibrational and collisional states of the surrounding medium. The result is

$$\frac{\partial P_M(t)}{\partial t} = \int_0^t ds \sum_N [w_{MN}(t-s)P_N(s) - w_{NM}(t-s)P_M(s)] \; . \tag{22}$$

Imitating the development of Förster[4] step by step one arrives at

$$w_{MN}(t) = \frac{2}{\hbar} \int_{W=0}^\infty \int_{w_N=0}^\infty \int_{w_M'=0}^\infty \int_{\Delta W=-\infty}^{+\infty} dw_M' \, dw_N \, dW \, d(\Delta W/\hbar) \cos(\Delta W/\hbar) tg'(w_M')g(w_N)$$

$$\times \left| u_{MN}(w_M', w_N; W_0 - W + w_M' + \tfrac{1}{2}\Delta W, W - W_0 + w_N + \tfrac{1}{2}\Delta W) \right|^2 \; . \tag{23}$$

The meaning of the various symbols, except for the replacement $k \to M$, $l \to N$, are identical to the ones appearing in the Förster theory[4] and it should be recalled that the matrix element of the Coulomb interaction u is evaluated partially in terms of energy-normalized states. M and N represent, as stated before, two sites or molecules. The vibrational contributions to the energy are denoted by w with a prime to denote the (electronically) excited state. Thus if the excitation resides on molecule M, the vibrational contributions of the two electrons involved are w_M' and w_N. The energy of the purely electronic excitation on either of the two molecules is W_0, and W and ΔW are abbreviations for the expressions $\{W_0 + \tfrac{1}{2}(w_M' - w_M + w_N' - w_N)\}$ and $(w_M + w_N' - w_M' - w_N)$, respectively. Finally the g's represent the products of the densities of states and thermal factors of the type $e^{-\beta w_M}$. The derivation of Eq. (23) is straightforward from the general theory developed in this paper as presented in Eq. (20) and the (model) assumptions of Förster stated explicitly in Ref. 4.

Equation (23) is the result of our general formalism at the (highly) coarse-grained level of description of the traditonal theory. It should be compared to Eq. (9) of Ref. 4 which is the well-known Förster result that forms of the basis for most discussions of excitation transfer. The two equations are identical except for the absence of $\pi \cos(\Delta W/\hbar)t\,d(\Delta W)$, the ΔW integration, and the

terms $\frac{1}{2}\Delta W$, in the expression for u_{MN} in Eq. (9) of Ref. 4. In the derivation of Eq. (23) the model assumptions of Ref. 4 have been postulated but the *Markoffian and the thermalization assumptions have not* been made. Thermal factors of the type $e^{-\beta w_M}$ appearing in $g(w_M)$, etc. appear also in our treatment in spite of the fact that the thermalization assumption is not made. They arise naturally from the coarse-graining operation. Of the two coarse-graining sums present in (20) one is responsible for the Fourier transformation of the interaction matrix elements. The other sum should normally cause bath parameters to appear in the final expressions. The only characteristic of the bath allowed to be reflected in this treatment however is the phase space of the bath-system aggregate. The states of this aggregate appear with equal weight in the second sum and this naturally gives weights $e^{-\beta w}$ in a summation over the vibra-

tional levels. It is the absence of the Markoffian approximation which gives rise to the ΔW terms in Eq. (23). It should be noted once again that the reduction of the GME with its $\mathcal{W}_{MN}(t)$ given by Eq. (23) to the usual PME of the traditional theory with its F_{MN} given by Eq. (9) of Ref. 4 is easily and immediately done by the replacement of $\cos(\Delta W/\hbar)t$ by

$$\delta(t)\left(\int_0^\infty ds\, \cos(\Delta W/\hbar)s\right) = \delta(t)\pi\delta(\Delta W/\hbar)$$

in Eq. (23). As we have remarked before, this replacement is valid only at large times and leads to results [e.g., Eq. (9) of Ref. 4] which are unable to provide a correct description of exciton transport at short times.

The application of our theory to unlike molecules gives the following interesting result involving oscillations of excitation between or among the molecules:

$$\mathcal{W}_{MN}(t) = \frac{2}{\hbar}\int_{W=0}^\infty \int_{w_N=0}^\infty \int_{w_M=0}^\infty \int_{\Delta W=-\infty}^{+\infty} dw_M' dw_N\, d(\Delta W/\hbar)\cos t(\Delta W - \Delta W_0)/\hbar$$

$$\times g'(w_M')g(w_N)\left|u_{MN}(w_M', w_N; W_0^M - W + w_M' + \tfrac{1}{2}\Delta W, W - W_0^N + w_N + \tfrac{1}{2}\Delta W)\right|^2 \quad , \quad (24)$$

where the energies of purely electronic excitation on molecules M and N are W_0^M and W_0^N, respectively, and $W_0^N - W_0^M = \Delta W_0$. Note that (24) predicts $\mathcal{W}_{MN}(t)$ to have the form

$$A(t)\cos\Delta W_0 t + B(t)\sin\Delta W_0 t \quad ,$$

wherein $A(t)$ and $B(t)$ are, respectively, the cosine and sine transforms of the same quantity. At long times, of course, the transfer rates predicted will be identical to those predicted by the usual form of the Förster theory with a shift ΔW_0 between donor and acceptor spectra.

V. CONNECTION WITH OPTICAL SPECTRA

An important contribution of Förster to the theory of exciton transport is the connection he established[4] between the formula for the rate F_{MN} obtained from the master-equation formalism and

the optical spectra of the molecules under study. This connection derives its importance from the fact that actual molecular aggregates are immensely complicated systems and a computation from formulae like the golden rule of Eq. (9) of Ref. 4, while possible in principle, are impossible in practice. It is only for a few drastically simplified models that such calculations can be carried out completely. Under the same general assumptions concerning the interaction used in the traditional theory we shall now show how our present theory generalizes the connection between the optical spectra and the transport characteristics.

With Förster,[4] Dexter[5] and others we take the interaction u to be given by the Coulomb interaction of the electrons suitably modified by the introduction of the "solvent" refractive index n. It is then possible to obtain from Eq. (23)

$$\mathcal{W}_{MN}(t) = \frac{4}{3\hbar n^4 R_{MN}^6}\int_{W=0}^\infty \int_{\Delta W=-\infty}^{+\infty} dW\, d(\Delta W/\hbar)\cos(\Delta W/\hbar)t \int_{w_M'=0}^\infty dw_M' g'(w_M')$$

$$\times \left|M(W_0 - W + \tfrac{1}{2}\Delta W + w_M', w_M')\right|^2 \int_{w_N=0}^\infty dw_N\, g(w_N)\left|M(w_N, W + \tfrac{1}{2}\Delta W - W_0 + w_N)\right|^2 \quad , \quad (23')$$

which should be compared to Eq. (9') of Ref. 4. Here R_{MN} denotes the distance between the sites M and N. The quantity $M(W)$ is the matrix element as defined by Förster, i.e., M^2 is proportional to the transition probability density on an energy scale. Recalling that the Einstein spontaneous transition probability density to the states between $(W_0 - W + \tfrac{1}{2}\Delta W + w')$ and $(W_0 - W - dW + \tfrac{1}{2}\Delta W + w')$ of the ground electronic state is given (except for constant factors) by

$$A(W_0 - W + \tfrac{1}{2}\Delta W + w', w') \sim (W - \tfrac{1}{2}\Delta W)^3 |M(W_0 - W + \tfrac{1}{2}\Delta W + w', w')|^2 \quad , \tag{25}$$

one may write down for the average over the thermal-equilibrium distribution function

$$\bar{A}(W - \tfrac{1}{2}\Delta W) \sim (W - \tfrac{1}{2}\Delta W)^3 \int_{w'=0}^{\infty} dw' g'(w') |M(W_0 - W + \tfrac{1}{2}\Delta W + w', w')|^2 \quad . \tag{26}$$

It is to be noted that $\bar{A}(W)dW$, which gives the number of quanta emitted per unit time per molecule in the energy range dW, represents the fluorescence intensity in that range. By following the discussion in Ref. 4 it is possible to obtain a similar expression for the absorption spectrum which shows that the extinction coefficient $\epsilon(W)$ is given (again except for constant factors) by

$$\bar{\epsilon}(W + \Delta W/2) \sim (W + \tfrac{1}{2}\Delta W) \int_{w=0}^{\infty} dw\, g(w) |M(w, W + \tfrac{1}{2}\Delta W - W_0 + w)|^2 \quad . \tag{27}$$

Observing that the integrals in Eqs. (26) and (27) are exactly the ones appearing in Eq. (23$'$) one may write the memory $w_{MN}(t)$ in terms of the absorption and emission spectra. The final expression is

$$w_{MN}(t) = \frac{3(\ln 10)\hbar^4 \bar{c}^4}{4\pi^2 n^4 N'} \frac{1}{R_{MN}^6} \int_{\Delta W=-\infty}^{+\infty} d(\Delta W/\hbar) \cos(\Delta W/\hbar)t \int_{W=0}^{\infty} dW \frac{\bar{A}(W - \tfrac{1}{2}\Delta W)\bar{\epsilon}(W + \tfrac{1}{2}\Delta W)}{(W - \tfrac{1}{2}\Delta W)^3 (W + \tfrac{1}{2}\Delta W)} \quad , \tag{28}$$

where $\bar{c}$ is the speed of light and $N' = 6.02 \times 10^{20}$ is the number of molecules per millimole (see Ref. 4). For like molecules we may use Levschin's law of mirror correspondence between the absorption and emission spectra and further reduce Eq. (28) to

$$w_{MN}(t) = \frac{3(\ln 10)^2 \hbar\, \bar{c}^2}{4\pi^4 n^2 (N')^2} \frac{1}{R_{MN}^6} \int_{\Delta W=-\infty}^{+\infty} d(\Delta W/\hbar) \cos(\Delta W/\hbar)t \int_{W=0}^{\infty} dW \frac{\bar{\epsilon}(W + \tfrac{1}{2}\Delta W)\bar{\epsilon}(2W_0 - W + \tfrac{1}{2}\Delta W)}{(W + \tfrac{1}{2}\Delta W)(2W_0 - W + \tfrac{1}{2}\Delta W)} \quad . \tag{29}$$

For the sake of comparison we repeat Förster's corresponding result for F_{MN} [Eq. (14) of Ref. 4].

$$F_{MN} = \frac{3(\ln 10)^2 \hbar \bar{c}^2}{4\pi^3 n^2 (N')^2} \frac{1}{R_{MN}^6} \int_{W=0}^{\infty} dW \frac{\bar{\epsilon}(W)\bar{\epsilon}(2W_0 - W)}{W(2W_0 - W)} \quad , \tag{30}$$

which is a consequence of our Eq. (29) under the Markoffian approximation.

Thus while the Förster analysis allows one to compute F_{MN} from the optical spectra through an evaluation of the integral in Eq. (30) [or the equation corresponding to (28) above] the algorithm suggested by our analysis is a little more involved. One does calculate the F_{MN} in Förster theory, and renames it $F_{MN}(0)$. One then shifts the two curves $W^{-3}\bar{A}(W)$ and $W^{-1}\bar{\epsilon}(W)$ on the frequency axis, the former by $+\tfrac{1}{2}\Delta W$ and the latter by $-\tfrac{1}{2}\Delta W$ [see Eq. (28)] and redoes the integral, symbolizing it by $F_{MN}(\Delta W)$. By repeating this operation for all values of ΔW one builds the entire curve. This $F_{MN}(\Delta W)$ is then the important quantity in our theory since its cosine Fourier transform yields the memory-dependent "transition rate" $w_{MN}(t)$:

$$w_{MN}(t) = \frac{1}{\pi} \int_{-\infty}^{+\infty} dz\, F_{MN}(z) \cos zt \quad . \tag{31}$$

The traditional theory is then seen to be represented by the zero-frequency region of $F_{MN}(z)$ which, by well-known theorems of Fourier analysis, corresponds to the long-time behavior of

$w_{MN}(t)$. Once again one notes that the replacement

$$w_{MN}(t) = \left(\int_0^{\infty} ds\, w_{MN}(s)\right) \delta(t) = \delta(t) F_{MN}(0)$$

(which is the Markoffian approximation) allows us to reobtain the Förster expression. Description of exciton transport at short times is influenced by $F_{MN}(z)$ at nonzero values of z and is thus seen to be outside the ken of the traditional theory. Insistence on using the PME at all times t presupposes flat absorption and emission spectra which are of course unrealistic and would lead to a catastrophe.

As an illustration of the memory function, we have computed $F_{MN}(z)/F_{MN}$ for transfer between anthracene molecules (Fig. 1). The absorption curve used was that of anthracene in cyclohexane solution[21] and the mirror symmetry relation was assumed for convenience.[22] The memory function

$$\phi(t) = (\pi F_{MN})^{-1} \int_{-\infty}^{+\infty} dz\, F_{MN}(z) \cos zt$$

is shown in Fig. 2. The memory vanishes well within a time corresponding to the usual picosecond
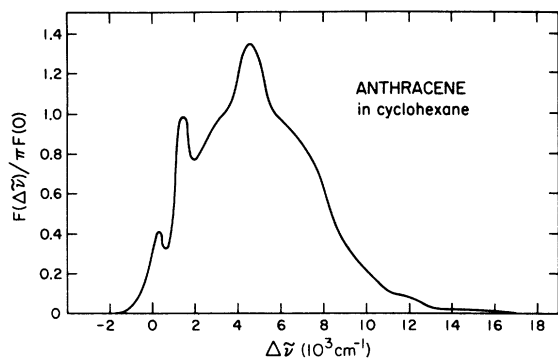
FIG. 1. Shape of the extended overlap integral $F_{MN}(\Delta\tilde{\nu})$ in the case of anthracene emission and absorption spectra in solution (see Ref. 21). The ordinate is normalized such that for the case of the usual Förster overlap integral ($\Delta\tilde{\nu}=0$) its value is $1/\pi$.

thermalization time, a fact which is of course related to the scale of the fine structure in the optical spectra. Sharper peaks in the spectra would mean smaller interactions with phonons and the environment and a correspondingly longer memory. It is instructive to examine the consequences of simulating the functions $\bar{A}(W)/W^3$ and $\bar{\epsilon}(W)/W$ appearing in (28), by Lorentzians: The resulting memory has the form

$$e^{-\alpha t}\cos(\Delta Et/\hbar) \quad,$$

where ΔE denotes the Stokes shift between the two curves. While the actual features of the anthracene spectra are reflected in Fig. 2, one indeed notes a decaying curve with an oscillating factor, since there is a Stokes shift in the spectra.

VI. DISCUSSION AND COMPARISON WITH OTHER TREATMENTS

We shall now carry out a brief comparison of the present formalism with other treatments of the problem of excitation transfer. Principal among the existing theories are (i) the one developed by Förster,[4] (ii) the Grover-Silbey[11] formalism, and (iii) the Haken-Reineker theory.[10] A detailed comparison between the Förster theory and the present formalism has already been carried out. It has been pointed out that since the PME forms the basis of the former, it is unable to describe exciton transport at short times. Our formalism achieves this through the memories $\mathcal{W}(t)$. As pointed out in Sec. IV, the Förster theory makes two assumptions in its development: (i) The *thermalization assumption* which states that the exciton undergoes complete intrasite (vibrational) relaxation ending in the achievement of a thermalized distribution after every hop and before the next hop away from the site, and (ii) the *Markoffian assumption* which is implied by the PME.

These two assumptions have totally different characters but appear to have been sometimes confused in the literature. The first has been questioned several times in the past, particularly by Dexter and collaborators.[23] The second assumption is the one that destroys the "wavelike" or "coherent" behavior and is the one that has been questioned by Robinson[24] among others. In the present theory neither of these assumptions is made. However, results formally equivalent to those of the thermalization assumption automatically appear as a natural consequence of the coarse graining at the level of the Förster description. The absence of the Markoffian assumption introduces cosine factors in expressions for $\mathcal{W}(t)$ and provides a prescription to construct the memory in the transport equation from the absorption and emission spectra of the molecules.

A detailed comparison of this theory to the Grover-Silbey (GS) and the Haken-Reineker (HR) formalisms can be made. The initial stages of these formalisms (in particular GS) are equivalent to our approach but the specific approximations and model assumptions cause differences to appear in the final transport equations. Here we shall merely point out these differences along with the similarities and display the expressions predicted by the respective treatments for the mean square displacement

$$\langle x^2(t)\rangle \equiv \int_{-\infty}^{+\infty} dx\, x^2 P(x,t)\Big/\int_{-\infty}^{+\infty} dx P(x,t) , \qquad (32)$$

which has been denoted by $R^2(t)$ and $n^2(t)$, respectively, by GS and HR.

For the sake of simplicity in the comparison we shall consider the one-dimensional (no-bias) continuum problem.[25] Inspection shows that Eq. (34) of GS may then be written
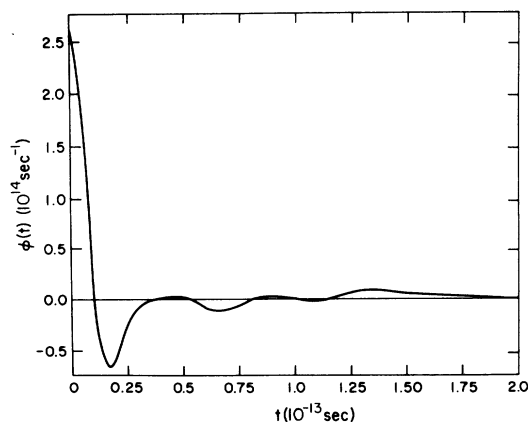

FIG. 2. Memory function $\phi(t)$, which is the cosine Fourier transform of the curve in Fig. 1. The ordinate is chosen in such a way that the curve is normalized to unity.

$$\frac{\partial P(x, t)}{\partial t} = 4J^2 a^2 \gamma_1(t) \frac{\partial^2 P(x, t)}{\partial x^2}$$

$$+ \text{``off-diagonal'' terms .} \qquad (33)$$

In the same context the corresponding HR equation is

$$\frac{\partial P(x, t)}{\partial t} = 4J^2 a^2 \gamma \frac{\partial^2 P(x, t)}{\partial x^2}$$

$$+ \text{``off-diagonal'' terms .} \qquad (34)$$

The theory developed in this paper yields for this situation [from Eq. (2)]

$$\frac{\partial P(x, t)}{\partial t} = \int_0^t ds\, \phi(t - s) D \frac{\partial^2 P(x, s)}{\partial x^2} + s(x, t) , \qquad (35)$$

and the traditional theory gives the diffusion equation [Eq. (16)]

$$\frac{\partial P(x, t)}{\partial t} = D \frac{\partial^2 P(x, t)}{\partial x^2} .$$

We have modified the notations of GS and HR slightly to avoid confusion.[26]

The traditional Eq. (16) has an instantaneous diffusion coefficient and no inhomogeneous term $s(x, t)$; the HR Eq. (34) has, like Eq. (16), an instantaneous diffusion constant but an inhomogeneous term appears; finally the GS Eq. (33) has an inhomogeneous term and a diffusion coefficient that is neither constant nor involves a convolution (i.e., a memory) but *is time dependent*. The special feature of our formalism (which it acquires from the use of projection techniques) is that the inhomogeneous term is given explicitly in terms of the initial condition and the (given) evolution operator. This is in contrast to the unknown inhomogeneous term in the GS or HR formalisms that require a complete solution of the problem before they can be given explicitly. Although ease in calculation is not necessarily assured by this fact, this may be considered a formal advantage of our theory (see also Ref. 16).

It can be shown that for the calculation of $\langle x^2(t) \rangle$, the inhomogeneous term is of minor importance in the GS Eq. (33) but makes the major part of the contribution to the results of the HR Eq. (34). By imposing proper boundary conditions at infinity it is possible to deduce the following equations for $\langle x^2(t) \rangle$.

GS:

$$\frac{d\langle x^2(t) \rangle}{dt} = 8J^2 a^2 \gamma_1(t) + \text{forcing term ;} \qquad (36)$$

HR:

$$\frac{d\langle x^2(t) \rangle}{dt} = 8J^2 a^2 \gamma + \text{forcing term ;} \qquad (37)$$

this theory:

$$\frac{d\langle x^2(t) \rangle}{dt} = 2D \int_0^t ds\, \phi(s)$$

$$+ \int_{-\infty}^{+\infty} dx\, x^2 s(x, t) ; \qquad (38)$$

traditional:

$$\frac{d\langle x^2(t) \rangle}{dt} = 2D . \qquad (39)$$

In view of the fact[11] that $\gamma_1(0) = 0$, the $t = 0$ value of the forcing term in Eq. (36) is

$$\left(\frac{d\langle x^2(t) \rangle}{dt} \right)_{t=0} .$$

The actual calculation[11] of $\langle x^2(t) \rangle$ from (36) is obviously dependent on the different values of this forcing term at different times. However, for obtaining the final expression [Eq. (42) of Ref. 11], which in our modified notation[26] is

$$\langle x^2(t) \rangle = a^2 [(2\alpha' + 4J^2/3\alpha')t$$

$$+ (4J^2/9\alpha'^2)(e^{-3\alpha't} - 1)] , \qquad (40)$$

it suffices to replace the forcing term by the constant $2a^2 \alpha'$ and $\gamma_1(t)$ by $(1 - e^{-3\alpha't})/6\alpha'$. With this substitution Eq. (36) gives $2a^2\alpha'$ as the initial value of $d\langle x^2(t) \rangle/dt$ and it is of interest to observe that this corresponds to a calculation from a diffusion equation like (16) with D given by $4J^2 a^2 \gamma_1(\infty)$. In terms of Eq. (38) one then has

$$2a^2 \alpha' = \int_{-\infty}^{+\infty} dx\, x^2 s(x, 0) .$$

Maintaining this value of the driving term in (38) constant for all times one then recovers the GS result for $\langle x^2 \rangle$ from our Eq. (38) by taking the exponential form $3\alpha' e^{-3\alpha't}$ for the memory $\phi(t)$.

By making the correspondence $\alpha' = \Gamma - \frac{1}{3}\gamma_0$, the results of the HR Eq. (37) [or of Eq. (4.2) of Ref. 10] may be written

$$\langle x^2(t) \rangle = a^2 [(2\alpha' + 4J^2/3\alpha' - \frac{4}{3}\gamma_0)t$$

$$+ (4J^2/9\alpha'^2)(e^{-3\alpha't} - 1)] . \qquad (41)$$

This expression may also be recovered from our Eq. (38) by assuming $\phi(t) = 3\alpha' e^{-3\alpha't}$ and

$$\int_{-\infty}^{+\infty} dx\, x^2 s(x, t) = C\theta(t)$$

as in the GS case but with $C = (2\alpha' - \frac{4}{3}\gamma_0)a^2$.

For the specific calculation of the mean-square displacement one thus sees that the HR and GS results correspond to the particular exponential form for the memory $\phi(t)$ in our formalism. As pointed out earlier the $F_{MN}(z)/F_{MN}$ curve possesses a structure that is reflected in the memory $\phi(t)$ (see Figs. 1 and 2). The results in Refs. 10 and 11 are thus equivalent to an approximation of the $F_{MN}(z)/F_{MN}$ curve by a Lorentzian [which, incidentally, means

that the driven form of a telegrapher's equation (17) is used for the probability evolution].

The GS and HR theories as well as the present formalism go beyond the Förster theory in that they can describe coupled wavelike and diffusive transport of excitons. In spite of their being entirely equivalent to our formalism in their beginning stages (particularly the GS theory which is purely dynamic, i.e., contains no stochastic element) their final results differ due to the specific approximations and model assumptions and as we have seen above correspond to an approximation to the memory curve,[27] which we obtain directly from optical spectra.

A non-Markoffian equation for the time evolution of the exciton probability which is based on a specific model calculation of Kudinov and Firsov[28] in the context of the polaron problem, has been written down by Paillotin.[12] It is a special case of our GME (8) in that it corresponds to a particular form of the memory function.

Two equivalent approaches have been used in investigations of exciton transport: the method of master equations and the method of random walks. A generalization of the former has been presented in this paper and it is therefore natural to ask whether the latter method can also be generalized in a similar manner. An extension of the Markoffian theory of random walks to continuous time situations already exists in the literature[29] and has been recently used[30, 31] for certain transport problems. It has been shown[32] that the memory $\phi(t)$ in a simplified GME of the form (14) above and the "pausing-time distribution function" $\psi(t)$ defined and used in Refs. 29–31 are related to each other through

$$\frac{d\psi}{dt} + \int_0^t ds\,\psi(s)\phi(t-s) = \phi(t) - \psi(0)\delta(t) . \qquad (42)$$

It can be further shown[20] that the Montroll-Weiss continuous-time random walk[29] can be extended to situations where the pausing-time distribution function $\psi(t)$ is not a universal function of sites and that an exact correspondence can be established between this generalization and the GME (8). With the relations

$$\sum_\mu \tilde{w}_{\mu\ell}(\epsilon) = \tilde{\phi}_\ell(\epsilon) , \qquad (43a)$$

$$\tilde{\psi}_\ell(\epsilon) = \frac{\tilde{\phi}_\ell(\epsilon)}{\epsilon + \tilde{\phi}_\ell(\epsilon)} , \qquad (43b)$$

$$\tilde{\mathcal{Q}}_{\ell\mu}(\epsilon) = \frac{\tilde{w}_{\ell\mu}(\epsilon)}{\epsilon + \tilde{\phi}_\ell(\epsilon)} , \qquad (43c)$$

the generalization of the MW random walk which is exactly equivalent to the GME (8) takes the form

$$P_\ell(t) = P_\ell(0)\left(1 - \int_0^t ds\,\psi_\ell(s)\right)$$

$$+ \int_0^t ds \sum_\mu \mathcal{Q}_{\ell\mu}(t-s)P_\mu(s) . \qquad (44)$$

The continuous-time random walk, which was originally introduced[29] as a specific model, is now seen to correspond exactly to the consequences of the Liouville equation under the initial diagonality condition. Exciton transport may thus also be analyzed within the framework of extended non-Markoffian walks.

The initial diagonality condition (IDC) imposed in the derivation of the GME (8) from Eqs. (1) or (2) requires comment. The situation in modern treatments of statistical mechanics is that this condition is essential to the derivation of the PME (and the consequent irreversible behavior) from microscopic dynamics. This is representative of the fact that the Schrödinger equation is *not* compatible with an approach to equilibrium under arbitrary initial conditions. The IDC is thus present in all traditional treatments of excitation transfer. It should be further emphasized that the IDC is used also in the modern treatments of exciton transport. It appears explicitly in applications[33] of the HR theory [see Eqs. (4) and (10) of the two Refs. 33] and implicitly in the GS treatment. This is evident from Eqs. (C4), (C1), and (40) of Ref. 11. The IDC can occur either due to random phases (the density matrix is obtained from the wave functions through an ensemble average) or in the pure case if the system is initially totally in a state η, i. e., $\rho_{\ell\mu} = \delta_{\ell,\mu}\delta_{\ell,\eta}$, where ξ, μ, η are the eigenstates.

The GS and HR treatments[11, 33] assume the latter more restrictive form of the IDC whereas the GME treatment uses the less restrictive random-phase condition. Furthermore within the framework of the present formalism it is possible to go beyond the IDC since $\mathcal{I}_\ell(t)$ is a *known* term in principle [see Eq. (5)]. On studying the structure of this term with the help of Eq. (6) or an approximate form which is analogous to (20), one reaches the following conclusions: (i) There are many situations when the $\mathcal{I}_\ell(t)$'s, even when not identically zero, decay much more quickly than the memories $w_{\ell\mu}(t)$ and a time range therefore exists when the GME can describe the transport correctly although it is still outside the reach of the PME; (ii) while the nature of the evolution of $w_{\ell\mu}(t)$'s depends solely upon the interaction, that of $\mathcal{I}_\ell(t)$'s depends upon the initial density matrix (in fact its off diagonal part) as well as upon V; (iii) the "coherent" or "wavelike" nature of exciton transport arises in general both from the memories $w_{\ell\mu}(t)$ and the initial term $\mathcal{I}_\ell(t)$; and (iv) the exact transport equa-

tion which is a "driven" GME (the "driving" or the inhomogeneous term is $\mathcal{J}_t$) can sometimes be transformed into a true GME without the driving term, which means that under these conditions the GME analysis is quite exact.

Note added in proof: Some further calculations concerning the mean-square displacement have now been published [V. M. Kenkre, Phys. Lett. A **47**, 119 (1974)]. In connection with the comparison of our formalism to the GS and HR theories, which appears in that reference as well as in Sec. VI above, it should be mentioned that the calculations concerning the initial values of $\langle x^2(t)\rangle$, etc., can be replaced by the simple statement that the $\langle x^2(t)\rangle$ given by the GS theory may be obtained from our formalism by approximating the actual memory $\phi(t)$ by the expression $3\alpha'e^{-3\alpha't} + (\alpha'a^2/D)\,\delta(t)$ and writing $D = 2J^2a^2/3\alpha'^2$. The HR expression is obtained in a similar manner.

The authors thank various colleagues for helpful comments on this and earlier versions of the work, especially Professor D. L. Dexter, Professor K. Lindenberg, Professor E. W. Montroll, Dr. R. Pearlstein, and Miss T. Rahman.

APPENDIX: SOME EXACT RESULTS IN A TWO-STATE MODEL

In this appendix we derive exact results for the case of a two-state system characterized by a Hamiltonian H given explicitly in the representation of the H_0 eigenstates (ξ, μ, etc.) as

$$H = \begin{pmatrix} \epsilon + \Omega & V_{12} \\ V_{21} & \epsilon \end{pmatrix} . \tag{A1}$$

The convolution term on the right-hand side of Eq. (2) may be written

$$\left(-\int_0^t ds\,\mathcal{P}Le^{-i(t-s)(1-\mathcal{P})L}(1-\mathcal{P})L\rho(s) \right)_{\xi\xi} .$$

To evaluate this term note that the following simple result can be established for the two-state system:

$$(1-\mathcal{P})LO = \begin{pmatrix} \Omega & 0 \\ 0 & -\Omega \end{pmatrix} O \tag{A2}$$

for any off-diagonal operator O. This shows that the action of the operator $e^{-i(t-s)(1-\mathcal{P})L}$ is extremely simple in this system. A straightforward calculation then yields the exact result

$$\mathcal{W}_{\xi\mu}(t) = 2|\langle\xi|V|\mu\rangle|^2\cos\Omega t . \tag{A3}$$

On comparing it with the approximate expression obtained from Eq. (19)

$$\mathcal{W}_{\xi\mu}(t) = 2|\langle\xi|V|\mu\rangle|^2\cos\omega t , \tag{A4}$$

one notes that the two results are identical except for the frequency of the cosine factors. The exact expression (A3) contains Ω, the difference between the first-order energies of the two states, whereas the approximate expression contains ω, which is the difference between the zero-order energies, i.e., the H_0 eigenstates. For a two-level system the approximate expression (19) is thus seen to simulate the exact Eq. (5) very closely and in fact reduces to the exact result in the case when V is off-diagonal in the H_0 eigenstates.

It is also interesting to observe that the analog of the wave equation for a two-state system is *exactly* obtained whenever the energies of the two states are identical (i.e., the memory is time independent) and when the $\mathcal{J}(0)$ term is zero (i.e., the system starts out completely in one of the states at $t=0$, or random phases apply at the initial instant). The conservation of positivity of P is assured by this initial condition.

The Zwanzig approximation used to derive (19) from (5) may also be used to obtain an expression for the inhomogeneous term in (2):

$$\mathcal{J}_t(t) = \text{Im}\,2i\sum_\mu e^{-it(E_\mu - E_\xi)}$$

$$\times\langle\xi|V|\mu\rangle\langle\mu|\rho''(0)|\xi\rangle , \tag{A5}$$

where Im represents the imaginary part and $\rho''(0)$ is the off-diagonal part of the density matrix at $t=0$. It may be noted from (A5) as well as (6) that $\mathcal{J}_t(t)$ is identically zero if $\rho(0)$ is diagonal. Equation (A5) shows that $\mathcal{J}_t(t)$ depends upon matrix elements of V as well as of $\rho''(0)$. The behavior of the inhomogeneous term thus depends on a combination of the interaction and the initial conditions. Equation (A5) has been derived from the Zwanzig definition of $\mathcal{P}$. On using our modified $\mathcal{P}$, the expression for $\mathcal{J}_t(t)$ is found to contain a coarse-graining operation which induces its decay in time in a manner analogous to the decay of $\mathcal{W}_{\xi\mu}(t)$. We shall here exhibit the exact and approximate expressions for $\mathcal{J}_t(t)$ derived with the Zwanzig $\mathcal{P}$ for our two-state system. These are respectively

$$\mathcal{J}_t(t) = X\cos\Omega t + Y\sin\Omega t \tag{A6}$$

and

$$\mathcal{J}_t(t) = X\cos\omega t + Y\sin\omega t , \tag{A7}$$

where

$$2(X+iY) = V_{12}\rho''_{21}(0).$$

Again the difference appears only in the frequencies.

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[26]Our α' and J correspond respectively to α and $\tilde{J}$ of GS and our γ to $1/4(\Gamma + \gamma_1)$ of HR.

[27]Note that the GS theory possesses much more generality than the particular form for $\gamma_1(t)$ [which corresponds to the exponential $\phi(t)$] might lead one to believe.

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